SYNOPSIS

Synthesis and Characterization of Yttrium Based Oxide Material for Security Ink Application

Submitting to

Research & Recognition Committee (RRC)

of

Faculty of Science

Swami Ramanand Teerth Marathwada University, Nanded

In

Subject Physics

Submitted by

Mr. Anil Hanmantrao Bodke

Research Student

School of Physical Sciences SRTMUN

Supervisor

Dr. N. S. Bajaj

Assistant Professor, Department of Physics

Toshniwal Arts, Commerce and Science College, Sengaon, Dist. Hingoli

(2024-2025)

SYNOPSIS OF THE PROPOSED RESEARCH WORK FOR Ph. D

Name of Candidate: Mr. Anil Hanmantrao Bodke

Title of Synopsis: Exploring yttrium based oxide materials for security ink application

1. Introduction

1.1 Counterfeiting and Its Impacts

Article without authorization and especially with intent to deceive or defraud. Usually, the word counterfeit is used for Fake banknotes and documents. Counterfeit products are fakes or unauthorized replicas of the real product. Counterfeit products are often produced with the intent to take advantage of the superior value of the imitated product. The word counterfeit frequently describes both the forgeries of currency and documents as well as the imitations of items such as clothing, handbags, shoes, pharmaceuticals, automobile parts, unapproved aircraft parts (which have caused many accidents), watches, electronics and electronic parts, software, works of art, toys, and movies.[1]

Counterfeit products tend to have fake company logos and brands, which results in patent or trademark infringement in the case of goods. They also have a reputation for being lower quality, sometimes not working at all, and sometimes containing toxic substances such as lead. This has resulted in the deaths of hundreds of thousands of people, due to automobile and aviation accidents, poisoning, or ceasing to take essential compounds (e.g., in the case a person takes non-working medicine).[citation needed] The counterfeiting of money, mostly paper money, is usually attacked aggressively by governments worldwide.

1.2 Anti-Counterfeiting Technologies and Luminescent Materials

With the rapid development of economy, the amount of fake products and information is rapidly increasing [2-3]. In such case, the information encryption and anti-counterfeiting technologies are essential to minimize the economic losses and protect public security [4], and have always been considered a major challenge. Up to now, there has been various designs for information encryption and anti-counterfeiting, which are based on different stimuli-responsive materials, such as the thermo-chromic photonic crystal [5], photo-responsive liquid crystal lasing materials [6], time-dependent luminescent materials [7-8], ani-sotropically shaped complex materials [9], circularly polarized luminescence (CPL) materials [10-12], and so on.

Among these intelligent response materials, the luminescent materials are most widely used, which could always be easily regulated by various external stimuli, such as the chemical reagent, heat, mechanical force, excitation light, and acid or alkaline. The output signals are abundant and can be ranged from the elementary parameters, such as the emission intensity and emission color, to the dynamic parameters, such as the time of emission duration and discoloration process.

Furthermore, the incident light has rich dimensions (wavelength, excitation duration, polarization, and power), and thus the multilevel stimulus can effectively improving the security level [13-14].

1.3 Security Ink:

Researchers have invented a nano-sized light emitting colloid material that could be used to mark security codes and design electronic devices1. Non-aqueous light-emitting colloids based on semiconductor nanoparticles have drawbacks such as toxicity of cadmium, harmful solvents and additives. To design safer aqueous colloids, the researchers used yttrium oxide and doped it with europium, a rare-earth element. This resulted in a transparent aqueous-stable colloid nanophosphor. A writing test showed the potential use of the transparent colloid (also called ink) for marking invisible security codes. The ink has potential application in protection of valuable documents and consumer products against fraud as also in optoelectronics, such as in the development of efficient light-emitting devices. "It can be used for making a transparent layer on silicon solar cell to modify solar spectrum and enhance the efficiency of solar cell," says lead researcher Bipin Kumar Gupta. The cost-effective technique could also be used for bio-markers and bio-labeling [15]

1.4 Importance of Luminescent Materials in Fabrication and Designing Security Ink

The fabrication and designing strategies of luminescent security ink play a key role for their commercial use in anti-counterfeiting applications. The major challenge in this area is to fabricate the luminescent ink having high stability, ease of availability of ink medium at low cost, good dispersion of luminescent 105 nano-materials in ink medium, high luminescent intensity of ink, convenience of printing and sticky nature of ink medium on different surfaces (viscosity around 3000 μP and better surface tension). Furthermore, it also important to understand the chemistry of luminescent security ink formation (whether the ink 110 is hydrophobic or hydrophilic in nature) prior to its potential use in printing of security codes/ bars on different types of surfaces [17-19] There are many different ways and materials used in the formation of luminescent security inks such as lanathanide based luminescent nano-materials (down-conversion, up-conversion and dual mode), luminescent quantum dots, and luminescent MOFs, plasmonics nano-materials and etc.

1.5 Choice of Lanthanide Oxide Based Luminescent Security Ink

out of these for current work it is decided to work with Lanthanide based luminescent security ink because In recent years the lanthanide based luminescent 60 nano-materials have gained huge attention due to their remarkable optical properties and wide range of applications in many potential areas such as luminescent security ink, optical displays, sensors, optoelectronics, laser cooling, bio-imaging and security applications etc. There are several potential advantages to use lanthanide based luminescent security inks for anti-countefeiting applications as compared to standard fluorescent inks, which normally produce visible emission when subjected to UV excitation. Furthermore, the lanthanide based luminescent inks exhibit both downconversion and upconversion processes in a single host lattice which makes them intrinsically more difficult to duplicate as compared to the standard fluorescent dyes. Additionally, another advantage of lanthanide based inks over the

commercially used fluorescent dyes is that former have sharper transitions without photo bleaching. Moreover, lanthanide based inks can be formulated to produce the correct color rendering index only under specific excitation power densities, making them even more difficult to duplicate the authentic read conditions. This section of review article will be mainly focused on fabrication and design of lanthanides based luminescent security ink including downconversion/downshift, upconversion and dualmode lanthanide based luminescent security inks.

1.6 Choice of Yttrium Based Materials for Current Work

Host matrix should have the ability to maintain the band width. properties of dopants for a of time, so it was decided to use Y_2O_3 better known as Yttrium oxide is with high melting point (2698k), high corrosion resistance, chemical durability photo chemical stability relatively high band gap (5.8ev) low phonon Frequency and ionic radii. Yttrium oxide is soluble in acids but only slightly soluble in water. This material com use as an additive in ceramics to improve hardness and has also high thermal, chemical and photo chemical. Stabilities. In addition to these properties it is also possible to control with precision the shape and size. Immense precision the shape and size of their particles and by modifying synthesis methods. Moreover yttrium oxide has large optical band gap (~5.5eV), high dielectric constant in the range between 14-18 and high refractive index n = 2. Y_2O_3 doped with rare earth ions is widely utilized in the field of luminescence such as high quality phosphors, up-conversion materials, transparent ceramics, catalysts, sensors, and biological labels. There are various phases of Y_2O_3. However, cubic phase of Y_2O_3 is one of the most studied oxide hosts for the solid state lasers, infrared ceramics, as well as for various other applications [19]

2. Review of work already done and recent studies

It was reported that metal oxide based - fluorescent inks have identical steady state emission properties, but they have distinctive and well separated emission lifetime which allows the authentication of security tags using exclusively fluorescent lifetime imaging. This can be applicable to variety of security protecting purposes and it can be extended to integrate fluorescent lifetime encoded metal oxide based CDs in multichannel bio imaging, high throughput flow cytometer and optical data storage. A photo-responsive supra-molecular polymer material was constructed and found that it facilitate fluorescence resonance energy transfer process via two component assembly strategy.

There are many Rare-earth ion-based metal oxides, possessing enormous potential for Yittrium Based Oxide Materials solutions. Many oxides of rare-earth ions directly or on-doping with other rare-earth ions shows luminescence characteristics. Some of them have been already applied and are discussed as follows

B. Kumar Gupta et. al. Eu^{3+} doped Yttrium (Y_2O_3) with an average diameter 5 nm developed luminescent transparent colloid that can be used as security link. Y^{3+} ion confining the growth of nano-phosphour using acid - catalyzed sol-gel method. Development of transparent aqueous - stable

Y_2O3: Eu^{3}+ colloidal solution are application relate to security ink code. (PL) Emission Yttrium oxide doped with Eu^{3+} having PL decay time range of a few milliseconds [18]

Ho^{3+} and Yb^{3+} co-doped Y_2O_3 phosphor combustion route and its up conversion by phosphors have good up conversion intensity and exhibited up conversion emission band of UV to NIR. Co-doping Yb^{3+} with Y_2O_3:Ho^{3+} phosphor have enhance the Ho^{3+} emission intensity ~ 290 times has a potential to be used as security application phosphor. [17]

Recently Manas Srivastava reported the codoping of yttria (Y_2O_3): Ho–Yb nanoparticles with Li which increases green light emission intensity applicable for security ink and bioimaging. The group reported that luminescence intensity of Ho^{3+} in the visible range decreases with doping of Yb^{3+} or Li^{+} due to energy transfer from Ho^{3+} to Yb^{3+}. Interestingly, luminescence peaks corresponding to Yb^{3+} (1000 nm) and Ho^{3+} (1200 nm) in the NIR range are also observed under 448 nm excitation. Peak observed at 1000 nm is related to the quantum cutting phenomenon. The quantum efficiency is found to be 180% from calculations. Its applications are extensively shown in different areas such as security ink, consignment identification, and bioimaging of muscle and bone through the NIR light up-conversion process. [20]

3. Importance of work

Currently many fraud marketing and fake product selling is happening in the market which directly and indirectly affecting the society. The work is focused with the brief motive of synthesis of luminescent yttrium based oxides for security ink application to overcome the false branding and marketing of products in the market. This directly and indirectly supports in the nation building as fake products are not quality approved and this may affects the health care of peoples. Also the fake branding loots peoples by selling fake products. Hence now a days, luminescent oxides are used as security ink materials in sensors in fingerprint imaging. Latent fingerprints, Printing ink, producing florescence material based holographic papers or those hidden from eye to overcome the threats of anti-counterfeiting.

4. Scope and Limitations:

a. Scope:

- Cost reduction in the synthesis of primary material will reduce the costing of entire process hence it has lot of potential to become benchmark for R & D sector.
- Department of Physics is the in only department in the Nanded university working in the field of fluorescent materials and its applications as an anti-counterfeiting materials so it has lots of space to aware peoples from the region to work on this current technology

b. Limitations:

- The main aspect of work is to produce low cost oxides with combination of methods, which requires accurate concentration of elements.

- To maintain exact application oriented crystallography is a tedious process
- iii. To maintain environment of laboratory as per the requirement of synthesis protocol.
- Production of ink or suitable colloidal solution using prepared materials to use as sequrity ink material is the biggest challenge in the work.

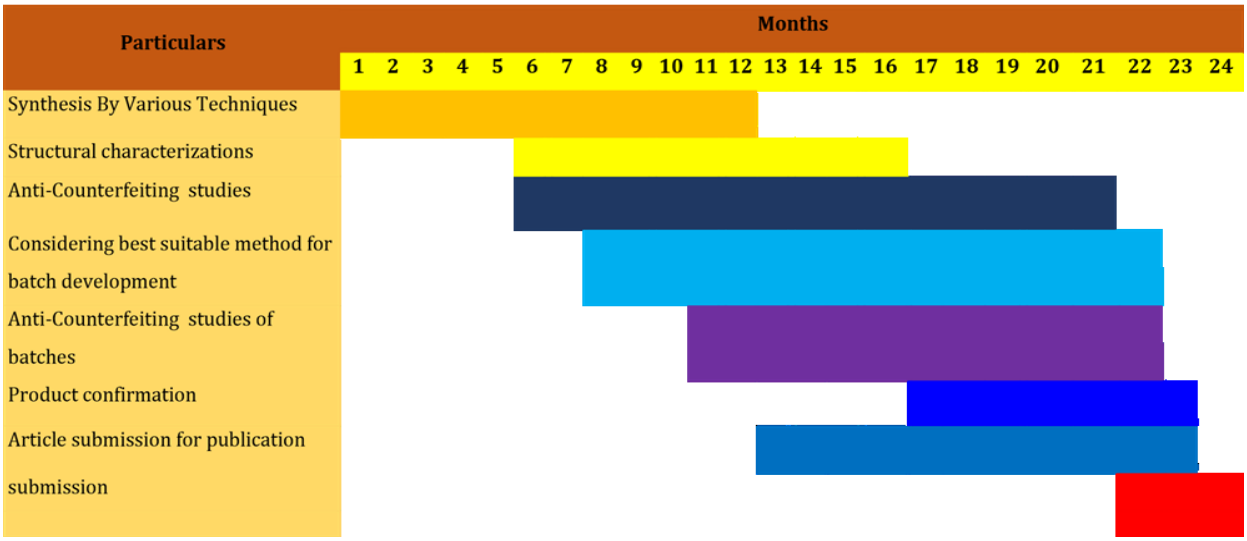
5. Objectives:

- Before preparing the draft of work exhaustive literature survey was done and it is noticed that there is less advancement in yttrium based metal oxide materials with reference to security ink applications. So it is decided to work with specific metal oxide and explore its low cost synthesis via combination of conventional and non-conventional synthesis processes.
- To characterize so obtained yttrium based metal oxides for standardization method through different techniques such as
    - X-ray Diffraction (XRD) for structural confirmation
    - Scanning Electron Microcopy (SEM) for morphological confirmation,
    - Raman or UV spectroscopy for Spectroscopic and Bond formation Confirmation
    - Photo luminescence Spectroscopy for applicability of product as anti-counterfeit materials
- Preparation of colloidal or ink based solution for utilization of prepared material in anti-counterfeiting techniques.
- Testing of prepared materials for their anti-counterfeit applications via screen printing technique or by ink jet printing technique.
- Repetition of process for bulk product delivery

6. Methodology detailing stepwise activities and sub-activities:

- Synthesis of proposed materials through various conventional and non-conventional techniques under small scale laboratory conditions.
- Structural characterizations of prepared materials for conformation
- Anti-Counterfeiting studies of prepared materials for their applications in various fields
- Considering best suitable method for batch development for large scale production
- Anti-Counterfeiting studies of batches for product uniformity Product confirmation & patent registration Article submission for publication to reputed journals

7. Work Plan


Particulars
Months
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Synthesis By Various Techniques
Structural characterizations
Anti-Counterfeiting studies
Considering best suitable method for batch development
Anti-Counterfeiting studies of batches
Product confirmation
Article submission for publication
submission

8. Relevance to State priorities:

In the recent years, there are number of problems related to counterfeit in drug industry, banking industry, insurance sector and range of products including fake university degrees, documents etc. There are number of products, which can be easily duplicated by simple processes and the product seems original that nobody doubts. Even the counterfeiting in currency is also a main problem in world's economy. So there are number of anti-counterfeit technologies including electronic combat mechanism are available in the market to prevent these antisocial activities. Though metal oxide based anti-counterfeit are very useful as per the security purpose. They can be used as printable inks to write down confidential documents or sign using, as material based holographic papers for product packaging, as latent fingerprints for locking confidential database etc. The main cause of using metal oxide based fluorescent material over other techniques as they are relatively easier to handle. These materials have diverse properties in different sources of excitation so that it can be a very good option to frame a security ink to overcome counterfeiting.

Date: 15/01/2024

Place: Sengaon

Research Scholar
Mr. Anil Hanmantrao Bodke

Supervisor
Dr. Nikhilesh S. Bajaj
Assistant Professor, Department of Physics
Toshniwal ACS College, Sengaon

References

1. "Physical Unclonable Functions in Theory and Practice", p. 46, by Christoph Böhm, Maximilian Hofer
2. Li, L., *Bus. Horizons* **2013,** *56*, 167-177.
3. Pyzik, O. Z.; Abubakar, I., *Nat. Rev. Dis. Primers* **2022,** *8*, 55.
4. Quan, Z.; Zhang, Q.; Li, H.; Sun, S.; Xu, Y., *Coordin. Chem. Rev.* **2023,** *493*, 215287.
5. Li, H.; Zhu, M.; Tian, F.; Hua, W.; Guo, J.; Wang, C., *Chem. Eng. J.* **2021,** *426*, 130683.
6. Xu, F.-F.; Gong, Z.-L.; Zhong, Y.-W.; Yao, J.; Zhao, Y. S., *Research* **2020,** *2020*, 65394.
7. Yang, T.; Wang, Y.; Duan, J.; Wei, S.; Tang, S.; Yuan, W. Z., *Research* **2021,** *2021*, 9757460.
8. Du, H.; Zhao, W.; Xia, Y.; Xie, S.; Tao, Y.; Gao, Y. Q.; Zhang, J.; Wan, X., *Aggregate* **2023,** *4*, e276.
9. Wang, X.; Feng, J.; Yu, H.; Jin, Y.; Davidson, A.; Li, Z.; Yin, Y., *Research* **2018,** *2018*, 7527825.
10. Guo, Q.; Zhang, M.; Tong, Z.; Zhao, S.; Zhou, Y.; Wang, Y.; Jin, S.; Zhang, J.; Yao, H.-B.; Zhu, M., et al., *J. Am. Chem. Soc.* **2023,** *145*, 4246-4253.
11. Hu, Y.; Huang, Z.; Willner, I.; Ma, X., *CCS Chem.* **2023**, DOI: 10.31635/ccschem.023.202302904.
12. Lin, S.; Tang, Y.; Kang, W.; Bisoyi, H. K.; Guo, J.; Li, Q., *Nat. Commun.* **2023,** *14*, 3005.
13. Yu, X.; Zhang, H.; Yu, J., *Aggregate* **2021,** *2*, 20-34.
14. Liu, S.; Liu, X.; Yuan, J.; Bao, J., *Research* **2021,** *2021*, 7897849.
15. https://www.nature.com/articles/nindia.2010.8
16. T. Blumenthal, J. Meruga, P. S. May, J. Kellar, W. Cross, K. Ankireddy, S. Vunnam, Q. N. Luu, *Nanotechnology*, 55 **2012**, 23, 185305.
17. P. Kumar, J. Dwivedi and B. K. Gupta, *J. Mater. Chem. C,* **2014**, 2, 10468-10475
18. B. K. Gupta, D. Haranath, S. Saini, V. N. Singh and V. Shanker, *Nanotechnology*, **2010**, 21, 055607.
19. R. Jayaramaiah, B.N. Lakshminarasappa, B.M. Nagabhushana, *Sensors and Actuators B: Chemical,* 173, **2012**, 234-238
20. M. Srivastava, S. K. Sahu, A. R. Singh, R. Agrawal, S. Kumar, R. Singh Ningthoujam, *ACS Appl. Nano Mater.,* 6, 22 **2023**, 20887–20898